Occurrence of Pesticides in Water, Sediment, and Soil from the Yolo Bypass, California

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ABSTRACT

The objective of this study was to evaluate the potential sources of pesticides to the Yolo Bypass, including those that could potentially impact critical life stages of resident fish. To assess direct inputs during inundation, pesticide concentrations were analyzed in water, and in suspended and bed sediment samples collected from source watersheds during high-flow events. To understand inputs from direct application on fields, pesticides were also measured in soils collected from several sites within the Bypass. Thirteen current-use pesticides were detected in water samples collected in 2004 with the highest pesticide concentrations observed at the input sites to the Bypass during high flows. Hexazinone and simazine were detected at all sites and at some of the highest concentrations. In bed and suspended sediments collected in 2004 and 2005, 13 current-use pesticides were detected, along with DDT and its metabolites. Trifluralin, DDE, and DDT were highest in the bed sediments, whereas oxyfluorfen and thiobencarb were highest in the suspended sediments. With the exception of the three organochlorine insecticides, suspended sediments had higher pesticide concentrations compared to bed sediments, indicating the potential for pesticide transport especially during high-flow events. Soil samples were dominated by DDT and its degradates but also contained a variety of current-use pesticides typically at lower concentrations. The types of pesticides detected in water and sediments were correlated with agricultural applications in each watershed. Understanding the distribution of pesticides between water and sediment is important in assessing their fate and transport within the Bypass, and in evaluating the exposure and potential effects to resident fish.

KEYWORDS

SUGGESTED CITATION

INTRODUCTION

Estuaries and floodplain systems offer important habitat, spawning grounds, and migration corridors for fish. Inputs of organic matter into the food web and decreases in predation or competition in these systems increase aquatic biodiversity (Corti et al. 1997; Winemiller and Jespen 1998; Junk et al. 1989). However, seasonal fluctuations in water level, sediment loads, and inputs of a wide variety of organic contaminants may influence the health and diversity of floodplain ecosystems.

Historically, much of Sacramento's Central Valley has been referred to as an "inland sea" during major storm events (Kelley 1989); however, today the Yolo and the Sutter bypasses function as floodplains for the Sacramento and Feather rivers. The Yolo Bypass drains
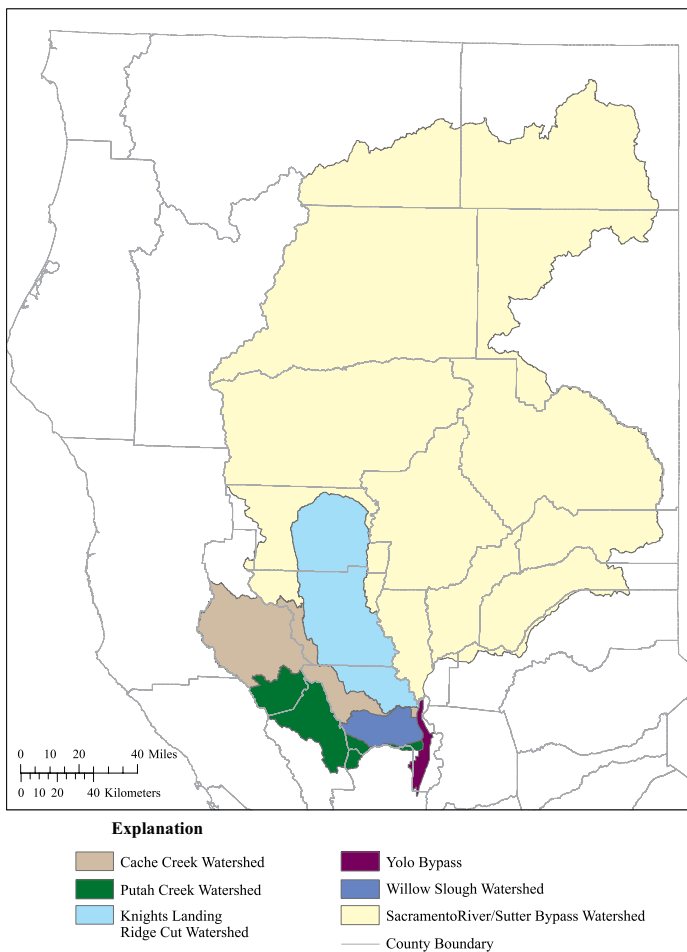

Figure 1. Yolo Bypass proper and the five source watersheds that drain into the Bypass under high-flow conditions.
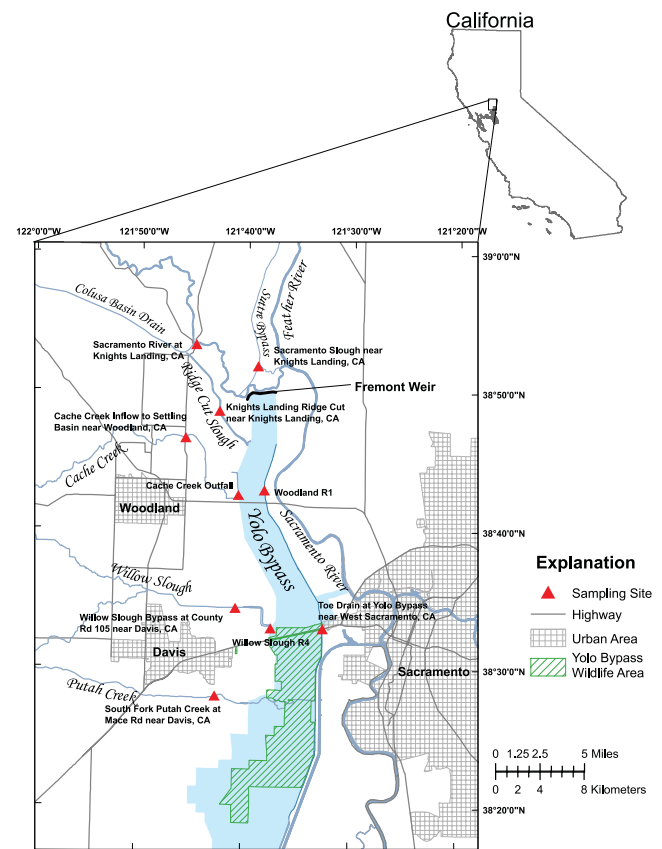

Figure 2. Input sources and location of sampling sites within the Yolo Bypass, CA.

south, roughly paralleling the Sacramento River, and can hold more than 4.5 times as much water as the Sacramento River. The Yolo Bypass was constructed between 1917 and 1924, during which a 65- km long, 240 km2 section of the Yolo Basin was delimited by engineered levees and weirs to divert flood waters away from Sacramento and other low-lying communities. Today, the Yolo Bypass floods in 7 out of 10 years with inundation occurring as early as October and as late as June, with flows most common between January and March. The duration of inundation within the Yolo Bypass can range from nearly four months to less than a week.

The Yolo Bypass receives water from five source watersheds as defined in the study (Figure 1) with seasonally varying hydrology that adds to the complexity of the floodplain system. The Bypass itself is relatively small, only 240 km^2; however, under high-flow conditions the watershed includes all of the input basins,

and dramatically increases in size to over 60,000 km². The largest watershed drains into the Bypass at the Fremont Weir and includes the Sacramento River, the Sutter Bypass and occasionally the Feather River (designated as the Sacramento River/Sutter Bypass watershed). Four smaller watersheds that enter on the west side of the Bypass are Knights Landing Ridge Cut, Cache Creek, Willow Slough, and Putah Creek (Figure 2). The Sacramento Weir, which conveys water from the Sacramento River (downstream of the Fremont Weir), (and occasionally the American River) is another potential input to the Bypass; however, this input did not affect our study because the weir was closed in 2004 during the high-flow sampling. Because the Yolo Bypass topography tilts from west to east, as well as from north to south, water flows toward the Toe Drain, a low-flow channel along the eastern edge of the Bypass. When the capacity of the Toe Drain (approximately 1,800–3,500 ft³/s, depending on location) is exceeded, lands adjacent to the Toe Drain are inundated.

During the dry season, when the Fremont and Sacramento weirs do not overtop, most of the water flowing into the Yolo Bypass comes from Knights Landing Ridge Cut, Cache Creek, Willow Slough, and Putah Creek. Cache Creek and Willow Slough transport limited amounts of municipal water from the cities of Woodland and Davis, respectively. Within the Bypass, most of the water from Cache and Putah creeks is shunted off for irrigation purposes and eventually drains across the Bypass into the Toe Drain, which is the primary source of perennial water within the Bypass. In the summer, there is also a net flow northward of tidally influenced water through the Toe Drain as far north as I-80, which is achieved via "tidal pumping." Water pumped northward is diverted and stored in Putah Creek behind the Los Rios Check Dam, a seasonal impoundment for agricultural and wildlife management uses.

Diverse hydrology, seasonally operated control structures, and frequent changes in management make the Yolo Bypass watershed a complex drainage area in which to assess the inputs of contaminants such as pesticides and mercury (Larry Walker Associates 2005). Agricultural fields and waterfowl management are dominant land uses within the Bypass, making up approximately 90% of the floodplain area. Land uses

in the remaining portion of the floodplain include marshes, ponds, and riparian and upland habitats.

A wide variety of crops are grown within and in the areas surrounding the Bypass, including alfalfa, beans, corn, melons, nuts (almonds and walnuts), orchards, rice, safflower, and tomatoes. This varied use results in the application of many different herbicides and insecticides. Thirty-three pesticides used in the Yolo Bypass and contributing watersheds were analyzed in this study (Table 1, Figure 1). Molinate and thiobencarb, two thiocarbamate herbicides, are used extensively on rice in the Bypass watershed (Crepeau and Kuivila 2000; California Department of Pesticide Regulation, 2004; Orlando and Kuivila 2004). Other pesticides with some of the highest use in the study area include

Table 1. Watershed size and pesticide application amounts (kg/year) for the Yolo Bypass and the five source watersheds that drain into the Bypass (California Department of Pesticide Regulation, 2004). Includes only the pesticides measured in the study.

	Yolo Bypass	Willow Slough	Putah Creek	Cache Creek	Ridge Cut	Sacramento/ Feather Rivers
Watershed size (km²)	243	697	1,685	2,957	4,339	350,364
Pesticide						
Alachlor	0	0	0	0	210	130
Atrazine	0	0	0	0	0	2,200
Bifenthrin	10	50	10	20	470	370
Carbaryl	640	340	20	690	2,700	5,500
Carbofuran	0	230	0	10	0	90
Chlorpyrifos	550	2,500	1,800	1,700	13,000	46,000
Cyfluthrin	5	130	10	20	110	60
Cypermethrin	120	100	2	10	340	340
DCPA	0	40	0	30	30	260
Deltamethrin	0	0	0	0	10	0
Diazinon	50	750	540	330	4,300	18,000
EPTC	0	0	0	580	620	1,800
Esfenvalerate	30	0	10	60	480	1,700
Ethalfluralin	460	0	370	1,400	3,700	1,400
Fenpropathrin	0	0	10	190	160	180
Hexazinone	1,900	3,700	220	600	3,000	9,800
Lambda-cyhalothrin	120	320	80	0	560	810
Malathion	260	560	50	340	4,300	8,000
Methidathion	0	0	0	0	260	2,000
Methyl parathion	80	0	0	0	250	3,700
Metolachlor	1,500	6,200	890	2,100	11,000	3,000
Molinate	1,100	290	0	140	24,000	120,000
Napropamide	170	310	340	120	860	2,000
Oxyfluorfen	160	1,600	1,100	2,400	10,000	11,000
Pebulate	380	300	440	450	780	470
Pendimethalin	0	80	70	140	2,500	5,300
Permethrin	240	110	20	150	2,200	2,700
Phosmet	1,800	0	0	70	8,200	10,000
Piperonyl Butoxide	0	0.005	0	0	0	0.002
Simazine	0	100	700	570	2,000	10,000
Tau-fluvalinate	0	0	0	0	30	50
Thiobencarb	9,000	7,000	0	470	54,000	130,000
Trifluralin	4,300	12,000	1,900	2,600	12,000	6,000

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Table 2. Pesticides detected in the study, their chemical classification, solubility, log K_{oc} as well as their primary uses in Northern California and peak month(s) of application.

Pesticide	Type [a]	Chemical Class	Solubility [b] (mg/L)	log K_{oc} [b]	Primary Use	Peak Application Month(s)
Atrazine	H	Triazine	28-33	1.95-2.81	Sudan grass	March
Bifenthrin	I	Pyrethroid	0.1	5.11-5.48	Structural, corn, cotton	May-July
Carbaryl	I	Carbamate	32-120	1.87-2.59	Melon, peach, pistachio	May-July
Chlorpyrifos	I	Organophosphate	0.3-2.0	3.77-4.5	Alfalfa, almond, walnut	May, August
DCPA	H	Benzoic Acid	<0.5-0.5	3.6-3.81	Broccoli, turf/sod	May-August
Diazinon	I	Organophosphate	60	3.18	Almond, walnut, fruit trees	December-July
EPTC	H	Thiocarbamate	344-370	2.23-2.45	Alfalfa, almond, bean	March-April; June-July
Ethalfluralin	H	Aniline	0.2-0.3	5.11	Sunflower	March-July
Hexazinone	H	Triazinone	298,000	1.3-1.73	Alfalfa	October-March
Lambda-cyhalothrin	I	Pyrethroid	0.005	6.8[c]	Alfalfa, rice, tomato	May-August
Methidathion	I	Organophosphate	220-250	2.29-2.76	Almond, walnut	January-April
Metolachlor	H	Chloracetanilide	488	2.0-25	Bean, corn, sunflower	March-June
Molinate	H	Thiocarbamate	88	1.9-2.3	Rice	April-June
Napropamide	H	Aryloxyalkanamide	73	2.48-2.85	Tomato, fruit trees	January-February
Oxyfluorfen	H	Diphenyl ether	0.116	2.6-2.8	Grape, almond, fruit trees	January-December
Pendimethalin	H	Aniline	0.3	2.49	Almond, cotton, walnut	January-December
Simazine	H	Triazine	2-6.2	2.11-2.15	Road side, almond, walnut	January-December
Tau-fluvalinate	I	Pyrethroid	0.103	4.26[c]	Carrot	May-June
Thiobencarb	H	Thiocarbamate	30	2.95	Rice	April-June
Trifluralin	H	Aniline	0.3-<1.0	2.5-4.5	Alfalfa, tomato	January-June

[a]H, Herbicide; I, Insecticide

[b]Mackay, D., Shiu, W. Y., Ma, K. C. 1997, Illustrated Handbook of Physical Chemical Properties and Environmental Fate of Organic Chemicals Vol 5. Pesticides. Lewis Publishers, Boca Raton, FL.

[c]log K_{ow}

(3) direct application of pesticides on crops grown in the Bypass. Understanding the fate of pesticides within this floodplain will help fisheries biologists assess the potential risks of long term exposure to juvenile and adult fish.

The resuspension and influx of pesticides into the Bypass during high-flow events may have an impact

chlorpyrifos, diazinon, hexazinone, metolachlor, oxy-fluorfen, simazine, and trifluralin (California Department of Pesticide Regulation 2004) (Table 1). Application of pesticides in the watersheds draining into the Bypass is seasonal, with a peak in application for most pesticides occurring between March and May (Table 2) (California Department of Pesticide Regulation 2004).

Pesticide use in the contributing watersheds has a direct impact on the Bypass itself, especially under high-flow conditions as pesticides move from the fields to surface waters in dissolved or sediment-bound forms. Suspended sediments entering the Bypass during high flows can be deposited and later resuspended. Pesticides attached to the suspended sediments may desorb during these events and become more bioavailable. Pesticides applied directly to soils within the Bypass during the dry season also have the potential to be resuspended and/or desorbed during high-flow conditions. The three potential sources of pesticide contamination to the Bypass are: (1) input of dissolved pesticides during inundation, (2) input of sediment-associated pesticides during inundation, and

on local fish populations. Limited information is available as to the long-term effects on fish from pesticide exposure in the Bypass during high-flow years when the pesticide flux from the surrounding watersheds is greatly increased. Fisheries studies conducted in the late 1990s suggest that the Yolo Bypass offers an important habitat to 42 fish species (Sommer et al. 2002). A few of the species found in the Bypass are year-round residents in the perennial waters; however, most use the Bypass as a migration corridor or as a rearing/spawning ground during the winter and early spring when it floods. Recent studies have shown that Chinook salmon (*Oncorhynchus tshawytscha*) increased in size substantially faster in the Yolo Bypass than in the Sacramento River (Sommer et al. 2001). This increase in growth rate was attributed to the warmer waters in the Bypass and the greater abundance and quality of food compared to the Sacramento River (Sommer et al. 2002; Sommer et al. 2001). Because the Yolo Bypass is an important fisheries habitat, some resource managers have proposed increasing the frequency and/or duration of local seasonal flooding of the Bypass. However, the impact of nonpoint source contamination of pesticides

Table 3. Surface water, bed sediment, suspended sediment and soil sampling sites in the Yolo Bypass and tributaries, California.

Site Name	Distance to Bypass (km)	Sample matrix collected
Sacramento River at Knights Landing, CA	9.1	Water
Sacramento Slough near Knights Landing, CA	2.0	Water
Knights Landing Ridge Cut near Knights Landing, CA	3.9	Water, Bed and Suspended Sediment
Cache Creek Inflow to Settling Basin near Woodland, CA	9.2	Water
Willow Slough Bypass at County Rd 105 near Davis, CA	4.7	Water and Suspended Sediment
Willow Slough Bypass R4	Within Bypass	Bed Sediment
South Fork Putah Creek at Mace Rd near Davis, CA	3.5	Water, Bed and Suspended Sediment
Toe Drain at Yolo Bypass near West Sacramento, CA	Within Bypass	Water and Bed Sediment
Field 27 North Sunflowers	Within Bypass	Soil
Field 27 South Sudan Grass	Within Bypass	Soil
Field 28 Tomatoes	Within Bypass	Water and Soil
Field 29 North Fallow Tomatoes	Within Bypass	Soil
Field 29 South Organic Tomatoes	Within Bypass	Water and Soil
Field 30 Wild Rice	Within Bypass	Water and Soil

to resident fish within the Bypass is still unknown. An ongoing study is investigating methyl mercury contamination in juvenile salmon in the Yolo Bypass and the Sacramento River (Marianne Kirkland, California Department of Water Resources, pers. comm.). Additional studies could be designed to investigate the effects of pesticides on fish within this area.

OBJECTIVES AND METHODS

The overall objective of the study was to evaluate the potential sources of pesticides to the Yolo Bypass during high- and low-flow events. The specific objectives of this study were to 1) assess the inputs of dissolved and sediment-bound pesticides to the Bypass during high-flow events in the winter and 2) measure the amounts of pesticides sorbed to agricultural soils within the Bypass during low-flow events in the summer.

Site Description

Sites were selected based on the major inputs to the Yolo Bypass. Surface water samples were collected from six sites that represent the five source watersheds

described above: Sacramento River at Knights Landing, CA (Sacramento River), Sacramento Slough near Knights Landing (Sacramento Slough), Knights Landing Ridge Cut near Knights Landing (KL Ridge Cut), Cache Creek Inflow to the Settling Basin near Woodland (Cache Creek), Willow Slough Bypass at County Rd 105 near Davis (Willow Slough), and South Fork of Putah Creek at Mace Rd near Davis (Putah Creek) (Table 3, Figure 2). All sampled sites were located as close to the Bypass as feasible. Because the Sacramento River/Sutter Bypass watershed upstream of Fremont Weir is so large (Figure 1), two sites were selected to represent the entire watershed (Sacramento River and Sacramento Slough). The Sacramento River
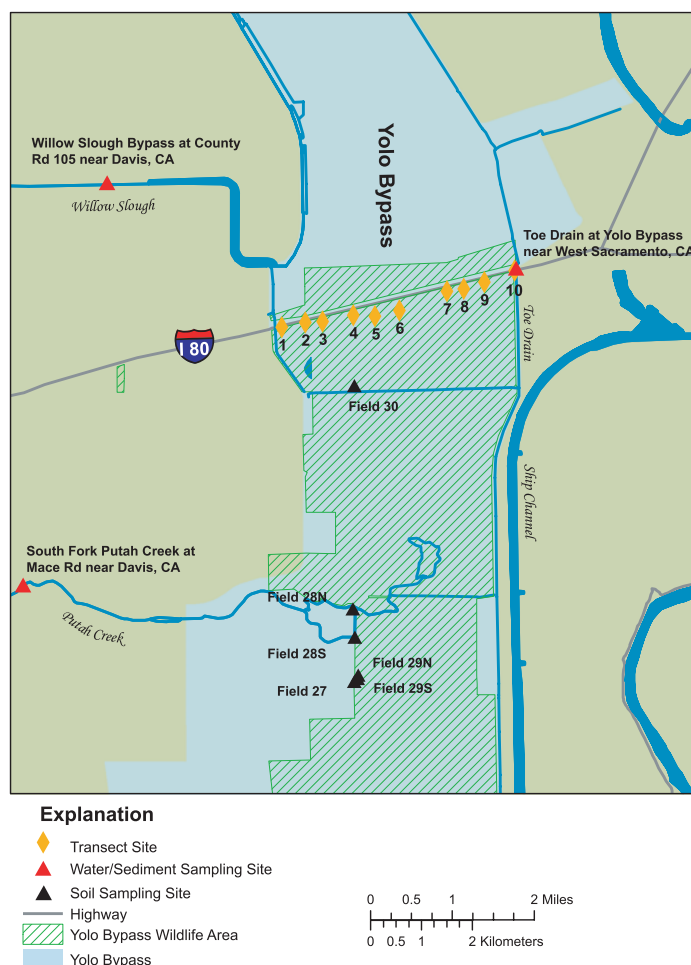
Figure 3. Map of 10 sampling locations along a transect conducted across the Yolo Bypass, CA on March 3, 2004, as well as soil sampling locations within the Bypass.

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site represents all water entering the Bypass from the Sacramento River, whereas the Sacramento Slough site represents inputs from the Sutter Bypass and potentially the Feather River depending on flow rates. Additional samples were collected from the Toe Drain at Yolo Bypass near West Sacramento (Toe Drain) located within the Bypass and 10 sites along one transect across the Bypass (Figure 3).

Sample Collection

The project was designed to assess the three potential sources of pesticide contamination to the Bypass. Accordingly, surface waters, sediments, and soils were sampled. All water and sediment samples were analyzed for pesticides at the U.S. Geological Survey California Water Science Center laboratory in Sacramento, California.

Water

Surface water sampling was conducted beginning in February 2004, following a significant rainfall and runoff event in the area (Figure 4), and continuing through the middle of March 2004. Water for the high-flow sampling was collected from February to March on a weekly basis from the six input sites. Surface water samples were also collected from 10 stations during a single transect across the width of the Bypass in early March (Figure 3).

Water samples were collected as mid-channel grabs from bridges using a weighted, two-bottle sampler at a depth of approximately 0.5-m directly into one 1-L baked, amber glass bottles. Transect water samples were collected by hand dipping 1-L baked, amber glass bottles just below the water surface at 10 stations spaced equally across the Bypass. All water samples were placed immediately on ice and transported to the laboratory.

Bed and Suspended Sediment

Another element of this study assessed the transport of pesticides associated with suspended sediments collected during high flows from the source watersheds
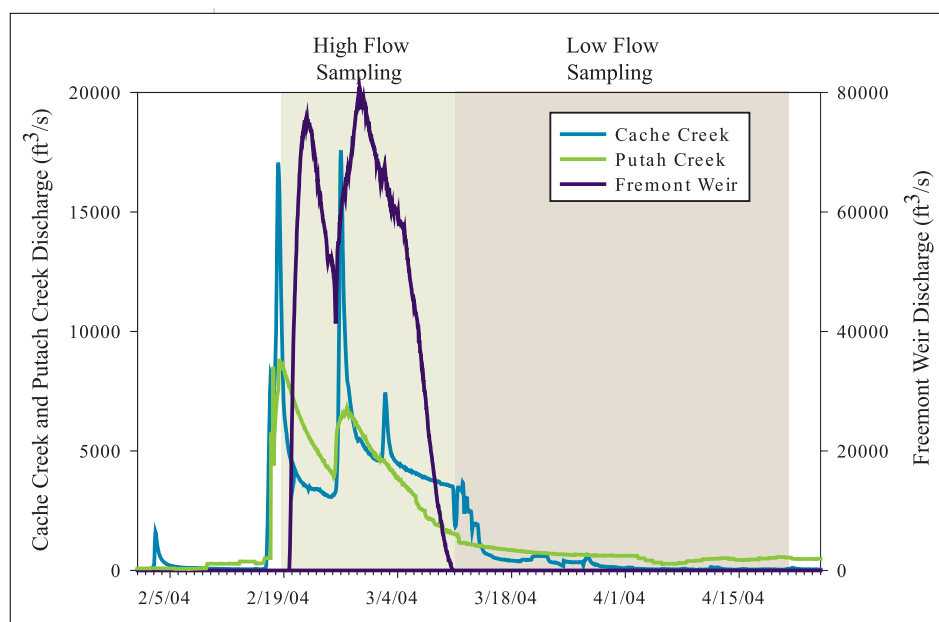

Figure 4. Discharge following a significant rainfall-runoff event at three inputs to the Yolo Bypass during 2004 high- and low-flow sampling events.

as well as from depositional bed sediments. Suspended sediments were collected during high-flow events in 2004 and 2005 from three sites: KL Ridge Cut (2004 and 2005), Willow Slough (2005), and Putah Creek (2004). Large volume water samples were collected and processed to isolate suspended sediments. At each site, approximately 200 L of water were collected using a peristaltic pump equipped with a stainless steel and Teflon inlet hose. Water was pumped at multiple stations across each channel profile, and at each station the inlet hose was suspended at multiple depths through the water column. Water at each site was collected and composited in 20-L stainless steel soda kegs. To isolate suspended sediment particles, samples were processed through a Westfalia continuous-flow centrifuge at a rate of two liters per minute using a peristaltic pump (Horowitz et al. 1989), within six hours of collection. In addition, a single 1-L water sample was collected from the centrifuge effluent and analyzed for dissolved pesticides.

Following centrifugation, the concentrated sediment and sediment-water slurry were removed and further dewatered by centrifuging for 20 minutes at 10,000

rpm using a high speed refrigerated centrifuge (Sorvall RC-5B centrifuge, DuPont Company, Wilmington, DE). The water separated during this step was decanted and the remaining sediments were placed in precleaned glass jars and stored frozen until analysis.

Bed sediment samples were collected in September 2004 by personnel from a local environmental consulting firm (Larry Walker Associates, Davis, CA). Samples were collected at two input sites (KL Ridge Cut and Putah Creek) and one site within the Bypass (Willow Slough R4) (Table 3, Figure 2). The Willow Slough sediment sampling site was located downstream from the site sampled earlier in the year for surface water and suspended sediments. Bed sediment was collected in 500-mL pre-cleaned glass jars from the top two centimeters of undisturbed stream bottom in areas of active deposition.

Soils

The third element of this study assessed the direct application of pesticides to agricultural fields within the Bypass. Soil samples were collected in late June 2005 from six sites within the Bypass with different agricultural practices (Table 3, Figure 3). Most of the soil sampling sites were close to one another and located such that they could be expected to have similar frequency and source of exposure from floodwater. Soil sites were chosen primarily by their location to one another within the Bypass and by crop type. Field 27 was divided into north and south sampling sites. The northern portion of the field (27 North) was planted with sunflowers, whereas the southern section (27 South) was planted with sudan grass. Field 28 was planted with tomatoes and surrounded completely by Putah Creek. Field 29 along the southern end of the Bypass was also divided into two sections. The northern section of the field (29 North) was planted with organic tomatoes and the southern section (29 South) was fallow but had been planted with tomatoes the previous year. Field 30 in the Yolo Bypass was freshly planted with wild rice and samples were collected following rice field flooding. Soil samples were a composite of the top 2 cm of the furrow near the plant and the ridge by the plant and were homogenized in a pre-cleaned glass jar.

Materials And Methods

Sample Preparation and Pesticide Extraction

Water samples were filtered through baked 0.7 μm glass fiber filters within 24 hours of collection. Terbuthylazine was added to each sample as a recovery surrogate and the samples were extracted onto C8 solid phase extraction cartridges. The cartridges were dried using compressed carbon dioxide, frozen, and stored at -20 oC. Prior to analysis, the cartridges were thawed, eluted with 9-mL of ethyl acetate, and concentrated for analysis. Deuterated polycyclic aromatic hydrocarbon (PAH) compounds were used as an internal standard and included d10-acenaphthene, d10-phenanthrene, and d10-pyrene (Crepeau et al. 2000).

Sediment samples were extracted based on methods described by LeBlanc et al. (2004) and Smalling et al. (2005). Briefly, wet sediments (~50% moisture) were extracted two times using a MSP 1000 (CEM Corporation, Mathews, North Carolina) microwave-assisted solvent extraction (MASE) with dichloromethane (DCM) and acetone (Jayaraman et al. 2001). The extracts were dried over sodium sulfate and reduced to 0.75 mL using a Turbovap II (Zymark Corporation, Hopkinton, Maryland). Sediment matrix was removed by passing the sample extract through two stacked solid phase extraction (SPE) cartridges containing 500-mg nonporous, graphitized carbon (Restek Corporation, Bellefonte, VA) and 500-mg Alumina (Varian Inc., Palo Alto, California) The cartridges were washed in tandem with 10 mL of DCM prior to sample extract addition. Compounds of interest were eluted off both SPE cartridges with 10 mL of DCM and collected as fraction 1 (F1). The carbon SPE was removed, and the Alumina SPE was eluted with 10 mL of ethyl acetate and DCM (50:50 v/v) and collected as fraction 2 (F2).

Both fractions were evaporated separately under a gentle stream of purified nitrogen gas (N-evap, Organomation Associates, Berlin, Massachusetts) to 0.5 mL and exchanged to ethyl acetate. Sulfur, found only in the F1 extracts, was removed using a gel permeation/high pressure liquid chromatography system (GPC/HPLC). The F1 and F2 extracts were reduced to 0.2 mL under a gentle stream of N_2 and the deuterated internal PAH standard mixture was added.
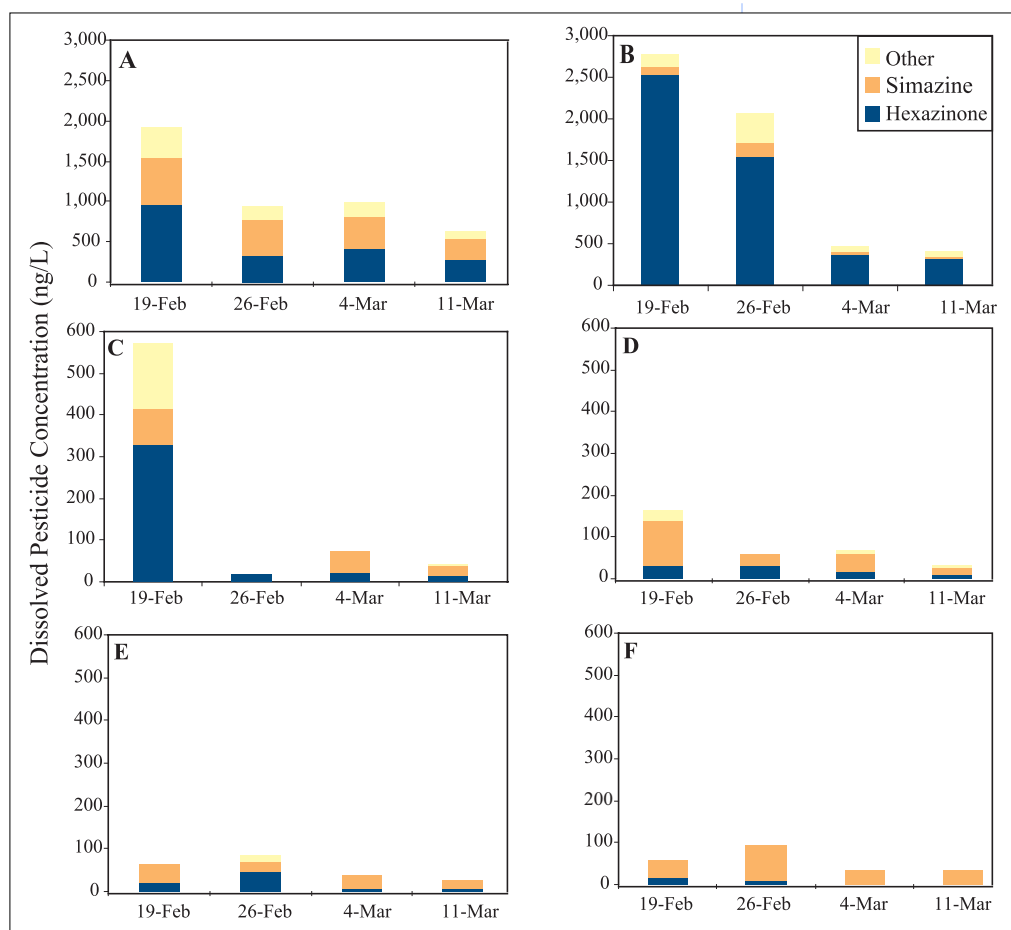
Figure 5. Change in dissolved pesticide concentrations over time during high-flow sampling in 2004 from (A) KL Ridge Cut, (B) Willow Slough, (C) Sacramento Slough, (D) Sacramento River (representing the Sacramento River/Sutter Bypass watershed), (E) Cache Creek, and (F) Putah Creek. Hexazinone and simazine were dominant in all watersheds; however, other types of pesticides detected varied by watershed and date. Note the differences in scales when comparing sites.

Gas Chromatography Mass Spectrometry

Water and sediment samples were analyzed for 27 and 41 pesticides, respectively, using a Varian Saturn 2000 gas chromatograph mass spectrometer (GC/MS) with ion trap detection. One microliter was injected into a DB-5 equivalent capillary column (Varian Walnut Creek, CA; Agilent Technology, Palo Alto, CA). The temperature of the injector was set at 275ºC and the trap, manifold, and transfer line temperatures were 220, 80 and 280ºC respectively. The GC oven program was as follows: 80ºC (hold 0.5 min); ramp to 120ºC at 10ºC/min; ramp to 300ºC at 3ºC/min (hold 5 min); ramp to 219ºC at 3ºC/min (hold 5 min); ramp to 300ºC

at 10ºC/min (hold 10 min). An eight point calibration curve was used to calibrate the instrument with concentrations ranging from 0.024 to 4.8 ng/µL. Intermediate-concentration check standards were injected every six samples to check instrument stability and verify that the response was within 10% of the standard curve. Complete details of the analytical method are described in Crepeau et al. (2000) and LeBlanc et al. (2004).

Quality Assurance/Quality Control

Dissolved pesticide concentrations were validated against a comprehensive set of quality control parameters including: laboratory and field blanks, matrix spikes, replicate samples, and surrogate recovery. No pesticides were detected in any of the blanks. Replicate samples analyzed were within 25% agreement for all pesticides detected. Matrix spikes were analyzed as part of the described method validation, with recoveries ranging from 80–120%. Terbuthylazine was used as a recovery surrogate, and the average percent recovery and standard deviation were calculated for each site. Sample data were excluded if the recovery of terbuthylazine was outside the mean plus or minus two standard deviations.

Sediment matrix spikes, method blanks and replicate samples were also processed for quality-control purposes. No pesticides were detected in any blank sample. Matrix spike percent recoveries ranged from 60 to 114%. Replicate samples were analyzed and the differences between replicates were less than 25% for all pesticides detected. Recovery of the sediment surrogate mixture was used to monitor the efficiency of each extraction. Average percent recoveries of ^{13}C-labeled

trifluralin, chlorpyrifos, p,p′-DDE and permethrin (cis/trans mixture) (Cambridge Isotope Laboratories Inc., Andover, Massachusetts) were 92 ± 10, 93 ± 9, 88 ± 13 and 95 ± 10, respectively.

The analytical method for surface water and sediment was validated by spiking seven replicates of a natural sample with a mixture of pesticides to determine method detection limits (MDLs) (U.S. Environmental Protection Agency 1992). MDLs for dissolved pesticides ranged from 0.6 to 7.2 ng/L and from 0.6 to 7.9 µg/kg for sediment-bound pesticides (Smalling et al. 2005). Analytes were identified at concentrations less than the MDL with lower confidence in the actual value, and are reported as estimated values.

RESULTS AND DISCUSSION

Input of Dissolved Pesticides During High Flows

Thirteen current-use pesticides were detected in surface water samples collected from the six input sites to the Bypass and the Toe Drain. Willow Slough, KL Ridge Cut, and the Sacramento Slough had the highest pesticide concentrations compared with the other sites, with values up to 2,500 ng/L (Figure 5). Most of the pesticides were detected in water from KL Ridge Cut and Willow Slough during the high-flow event (February through March) and at the Toe Drain
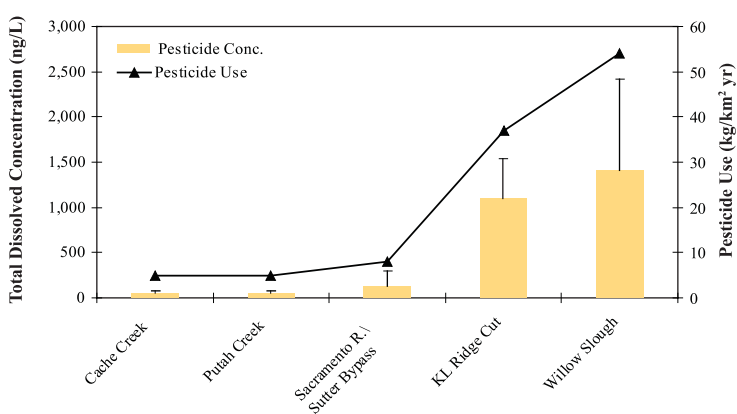

Figure 6. Total dissolved pesticide concentration (avg ± SD) in each watershed was significantly correlated with pesticide use normalized to watershed area in 2004. Sacramento River/Sutter Bypass represents an average of concentrations from Sacramento River and Sacramento Slough sampling sites.

between February and April 2004. In contrast, Cache Creek, Putah Creek, and the Sacramento River had the lowest number of pesticides detected and some of the lowest pesticide concentrations (Table 4, Figure 5).

The inputs of dissolved pesticides to the Yolo Bypass vary by watershed and depend on a variety of factors, such as timing of application, amount of pesticides applied, rainfall, and flow. The watersheds themselves also differ in size, land-use, and the types of pesticides applied. To account for this large variability in the sizes of the five watersheds, total and individual pesticide use must be assessed based on area; therefore, pesticide use in each watershed was normalized to watershed area (Table 1). The total pesticide concentration in each watershed was calculated based on an average of the four high-flow sampling time points at each sampling site. For the Sacramento R./Sutter Bypass watershed, total pesticide concentration was based on an average of the Sacramento River and Sacramento Slough sites at each of the four time points. The spatial distribution of dissolved pesticide concentrations was significantly correlated with pesticide application amount in each watershed (p-value <0.05) (Figure 6).

The amount of pesticides applied in each watershed, their physical–chemical properties (i.e. sol-

Table 4. Dissolved pesticides detected in surface water from each watershed during high-flow sampling. "X" represents at least one detect during the four sampling time points.

	Cache Creek	Putah Creek	KL Ridge Cut	Willow Slough	Sacramento River/Sutter Bypass [a]
Pesticide					
Carbaryl					X
Diazinon			X	X	X
EPTC					X
Hexazinone	X	X	X	X	X
Methidathion			X		
Metolachlor	X		X	X	X
Molinate			X		X
Napropamide			X	X	
Oxyfluorfen			X	X	X
Pendimethalin			X		X
Simazine	X	X	X	X	X
Thiobencarb			X	X	X
Trifluralin	X		X	X	X

[a] Includes Sacramento River and Sacramento Slough sampling sites

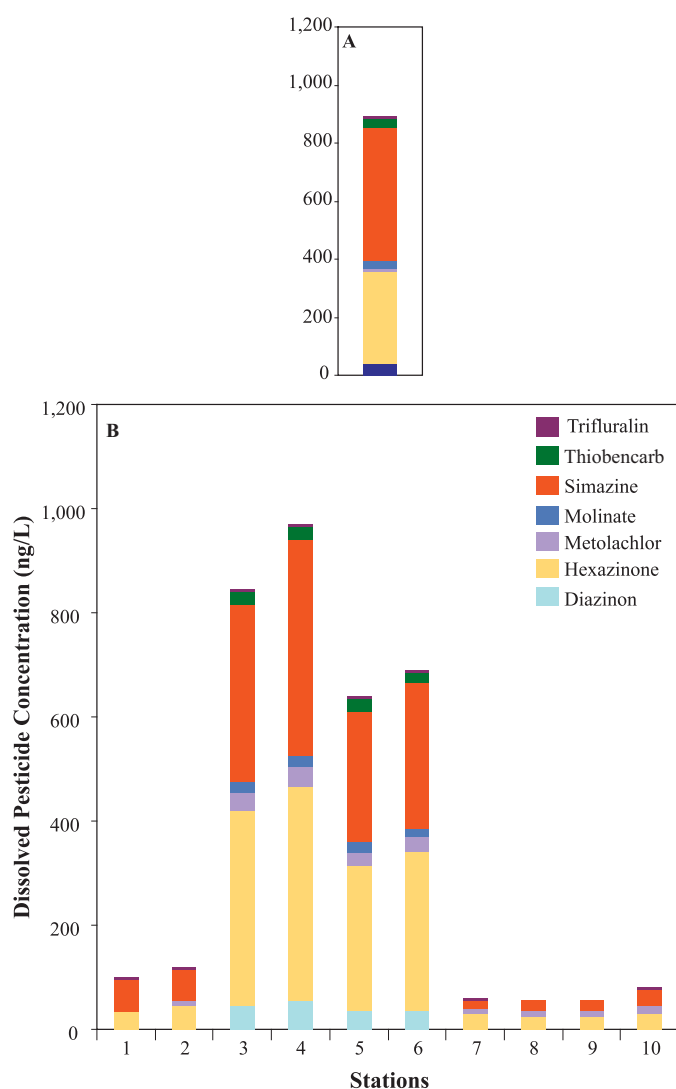**SAN FRANCISCO ESTUARY & WATERSHED SCIENCE**

Figure 7. Dissolved pesticide concentrations in samples collected from (A) KL Ridge Cut February 24, 2004 and (B) nine stations and the Toe Drain along a transect across the Yolo Bypass on March 3, 2004.

ubility and log K_{oc}), as well as the timing and the location of application (Table 2) are important in understanding the detection and distribution of the individual pesticides within each watershed. Hexazinone and simazine were the dominant pesticides detected in each watershed, but their concentrations varied by site and decreased over time (Figure 5). Hexazinone, applied primarily to alfalfa, was detected most frequently and at some of the highest concentrations, which can be attributed to its high water solu-

bility (33,000 mg/L) and high use in each watershed. The normalized use of hexazinone was highest in the Willow Slough watershed followed by KL Ridge Cut, whereas use in the other three watersheds was much lower. Simazine, on the other hand, has widespread agricultural and nonagricultural applications, such as weed control along roadways throughout Northern California (Domagalski 1996; California Department of Pesticide Regulation 2004). Simazine is used during much of the year; however, its use is highest during the winter (Table 2). Studies in the San Joaquin River and the Sacramento River Valley have detected elevated concentrations of simazine throughout the year with a pulse in the winter during storm events (Domagalski 1996; MacCoy et al. 1995). Similar trends were observed during the high-flow sampling events in this study; simazine was detected at some of the highest concentrations in KL Ridge Cut and Willow Slough and was detected frequently at all sites throughout the study period (Figure 5).

During the Bypass transect sampling in early March 2004 (Figure 3), seven current-use pesticides were detected in the water samples. Hexazinone and simazine were detected at all stations across the transect and had the highest concentrations (Figure 7). Water from stations 3, 4, 5, and 6 had significantly higher pesticide concentrations compared with the other stations. The concentrations and the pesticides detected (diazinon, molinate, and thiobencarb) at stations 3 through 6 are similar to dissolved pesticides detected at KL Ridge Cut and offer a distinct 'fingerprint' of source water from that watershed (Figure 7). Stations 1 and 2 represent water from Cache Creek, whereas stations 7 through 9 represent the Sacramento River/Sutter Bypass. Inferences from the transect data along with previous studies suggest little mixing of the water masses moving through the Bypass. Archived aerial photographs indicate distinct water masses that are visible across the length of the Bypass (Sommer et al. 2001). Mixing in the Bypass is hypothesized not to occur because eddies that would otherwise mix the waters are limited by the relatively shallow mean water depth even during extremely high-flow conditions (Sommer et al. 2001). Therefore, water collected at each transect station represents distinct water masses from three of the five sources and the

Toe Drain. The lack of mixing of source waters in the Bypass is important in understanding the fate and transport of the pesticides entering under high-flow conditions. If the water masses do not mix, as indicated by previous studies and confirmed by this one, then there is no dilution within the Bypass under high-flow conditions.

The highest concentrations of dissolved pesticides enter the Bypass from the source watersheds during the first high-flow event following winter pesticide application (Figures 4 and 5). For the most part, pesticide concentration and the number of pesticides detected in each watershed decreased from February to April, especially in water from KL Ridge Cut and Sacramento and Willow Sloughs. Most of what was applied in the summer that has not degraded or washed off during irrigation as well as pesticides applied early in the winter, such as the dormant spray pesticides, have the potential to impact the Bypass during the first rain event in the winter (Domagalski et al. 1997). Dissolved pesticides are considered the most bioavailable and may have the greatest impact on the aquatic community (Hamelink et al. 1994; Mackay and Fraser 2000). The pulse of dissolved pesticides during high-flow events is short lived; however resuspension and mobilization of sediment-bound pesticides during these events may also be important within the Bypass.

Pesticides Associated with Suspended and Bed Sediments

In the six bed sediment samples and four suspended sediment samples collected in 2004 and 2005, 13 current-use pesticides were detected. Thiobencarb and trifluralin were detected most frequently (80%) and at some of the highest concentrations (both at 24 μg/kg dry weight) (Figures 8 and 9). Oxyfluorfen, was detected at the highest concentration in Willow Slough suspended sediment (50 μg/kg), whereas bifenthrin, carbaryl, DCPA, and napropamide were detected at the lowest concentrations and frequency across all sites. The pesticides detected in the sediment samples were
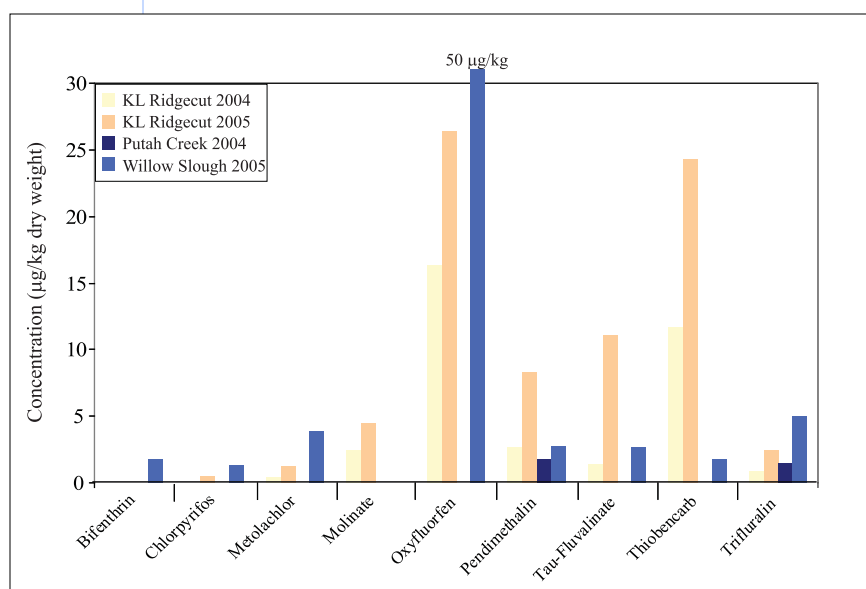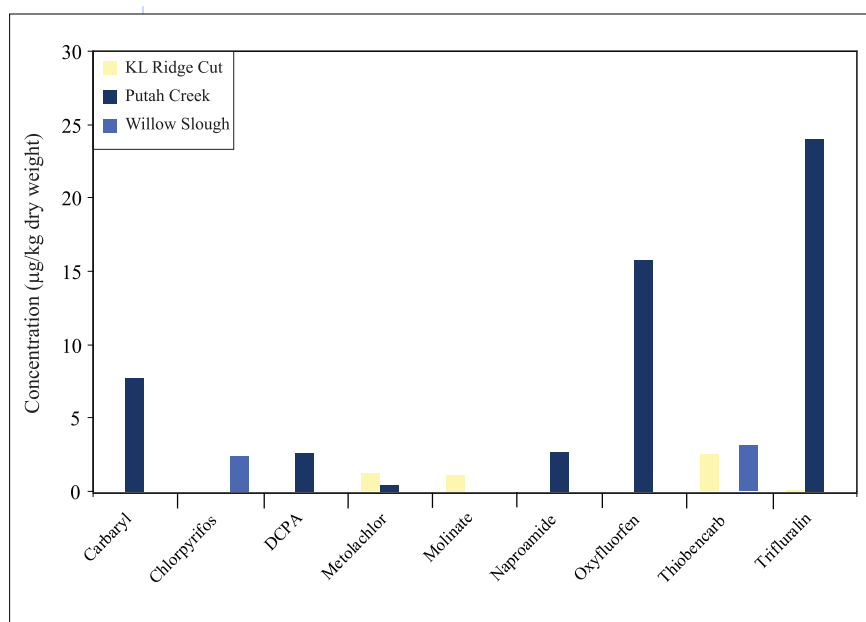

Figure 8. *(top)* Concentrations of current-use pesticides in bed sediments collected in September 2004.

Figure 9. *(bottom)* Concentrations of current-use pesticides in suspended sediments collected February 2004 and January 2005.

typically different from those in the surface water samples because the distribution between water and suspended sediment depends on the physical–chemical properties, such as solubility and log Koc, of each pes-

ticide. For example, surface water was dominated by hexazinone, simazine, and metolachlor, pesticides with higher solubilities and lower log K_{oc}, whereas oxyfluorfen, thiobencarb, and trifluralin were detected primarily on the sediments. In addition, compounds such as bifenthrin and tau-fluvalinate with a log K_{oc} >5 were only detected on sediments. These two pyrethroid insecticides were detected in suspended sediment samples from KL Ridge Cut and Willow Slough but were not detected in the bed sediments, indicating a potential shift in use over the past year. In these relatively rural watersheds, the source of these two pyrethroids is unclear because their registered agricultural use in the watersheds, especially for tau-fluvalinate, is very low and there is very little urban input. However, the agricultural use of bifenthrin and tau-fluvalinate has increased over the past several of years, primarily between 2003 and 2004, which may explain the increase in concentration of tau-fluvalinate in suspended sediments from KL Ridge Cut in 2005 compared with 2004. Pesticide use, along with physical–chemical properties, such as log K_{oc} and solubility, plays a significant role in determining the fate of the different types of pesticides in the Yolo Bypass watershed.

The suspended sediments had higher concentrations and a greater number of pesticides detected compared to the bed sediment (Figure 9). Most suspended sediments enter a system as fresh sediments in the winter, move from the fields to the rivers during high-flow events, and then have the potential to be deposited as the flows begin to decrease. A direct comparison of bed and suspended sediments can not be made in this study since they were collected at two different times of the year. However, it is interesting to note that the pesticides associated with suspended sediments are considered less degraded than those associated with bed sediments, especially in this study. The exception was Putah Creek where bed sediments had relatively high total pesticide concentrations (~ 60 µg/kg) compared with the other sites, whereas the suspended sediments had some of the lowest concentrations. It has been hypothesized that Putah Creek received fresh sediment deposits from agricultural fields via overland flow of irrigation water during

the summer and fall, which would explain the less weathered profile and the higher concentrations of current-use pesticides compared with the other sites sampled. All other sampling locations were dry during the summer and fall and had no direct or indirect inputs of sediments except during high-flow events in the winter. The low pesticide concentrations associated with the suspended sediments, on the other hand, were attributed to a trapping and dilution effect of the upstream dam and reservoir, in conjunction with the extreme high-flow conditions. At the time of sampling, Monticello Dam was spilling water from Lake Berryessa into Putah Creek, releasing large volumes of water with very low suspended sediment concentrations. We hypothesize that either the first flush in Putah Creek was missed altogether, or the sediments sampled originated in a different portion of the watershed. The suspended sediment concentration in Putah Creek water was only 250 mg/L during the high-flow event compared with the other input sites, where concentrations ranged from 400 to greater than 1,000 mg/L (Smalling et al. 2005). The suspended sediments sampled from Putah Creek in 2004 had relatively low pesticide concentrations similar to the surface water,

Table 5. Pesticide concentrations (Ìg/kg dry weight) in soils collected from agricultural fields within the Yolo Bypass, CA in June 2005.

	Field 27 North	Field 27 South	Field 28	Field 29 North	Field 29 South	Field 30
Compound						
Atrazine	*nd*	*nd*	*nd*	*nd*	*(1.0)*	*nd*
EPTC	*(1.0)*	*nd*	*nd*	*1.6*	*nd*	*nd*
Ethalfluralin	*242*	*nd*	*nd*	*nd*	*nd*	*nd*
Lambda-cyhalothrin	*nd*	*nd*	*6.2*	*nd*	*nd*	*nd*
Metolachlor	*9.2*	*8.2*	*397*	*12.8*	*nd*	*nd*
Molinate	*nd*	*nd*	*nd*	*nd*	*nd*	*10.5*
Napropamide	*nd*	*nd*	*46.0*	*4.3*	*nd*	*nd*
Oxyfluorfen	*27.3*	*16.2*	*23.3*	*7.6*	*nd*	*nd*
Pendimethalin	*nd*	*nd*	*3.3*	*nd*	*nd*	*nd*
Prometryn	*5.3*	*2.5*	*4.1*	*6.2*	*10.5*	*2.5*
Thiobencarb	*nd*	*nd*	*nd*	*nd*	*nd*	*3.3*
Trifluralin	*24.0*	*20.8*	*251*	*16.6*	*6.4*	*4.0*
p,p'-DDD	*38.5*	*44.8*	*60.6*	*30.0*	*3.1*	*2.2*
p,p'-DDE	*329*	*387*	*541*	*137*	*13.4*	*7.0*
p,p'- DDT	*116*	*132*	*185*	*97.6*	*6.9*	*(1.4)*
Σ DDT	*484*	*564*	*786*	*264*	*23.0*	*11.0*

nd = not detected
( ) = values below MDL and are estimated

indicating rapid flushing of the area with clean pulses of water released from Lake Berryessa.

Direct Application of Pesticides in the Yolo Bypass

The third type of input is pesticides applied directly to soils within the Bypass. Six agricultural field soils were sampled in June 2005. Twelve current-use pesticides were detected at concentrations ranging from <1 to 397 µg/kg (Table 5). The pesticides detected on each field can be correlated with the types of crops and the pesticide application. For example, metolachlor, napropamide, and trifluralin applied to tomatoes were approximately 100 times higher in soils from field 28 than soils from the other sites. Furthermore, ethalfluralin, applied to sunflowers, was detected only in samples from field 27 north, whereas lambda-cyhalothrin, applied to tomatoes, was detected only in soils from field 28. Thiobencarb and molinate, used extensively on rice (Crepeau et al. 2000), were only detected in soils from field 30. However, in 2005, field 30 was planted with wild rice, which does not require application of molinate and thiobencarb; therefore, these two compounds likely persisted in soils from a previous application. Molinate and thiobencarb were also detected in other bed sediment samples in this study from areas where these pesticides were not currently being applied. These two compounds have been detected during the winter in suspended sediments throughout the San Joaquin River and the Delta region and are considered to be moderately persistent in sediment and soils (Bergamaschi et al. 2001; Johnson and Lavy 1995; Soderquist et al. 1977).

DDT and Degradates in Sediments and Soils

Trace levels of DDT and/or its degradation products were found in most bed and suspended sediment samples and all soil samples with ∑DDT concentrations ranging from <10 to 786   g/kg (Figure 10). Total DDTs were highest in the Yolo Bypass soil samples and Putah Creek bed sediments and lowest in the suspended sediments samples. Studies have shown that DDT degrades to DDD under anaerobic conditions and to DDE under aerobic conditions (Foght et al. 2001; Hitch and Day 1992; Pereira et al. 1996). The concentration of DDE was greater than DDD or DDT in all but two Yolo Bypass bed sediment samples. Ratios of DDE/DDT in field soil
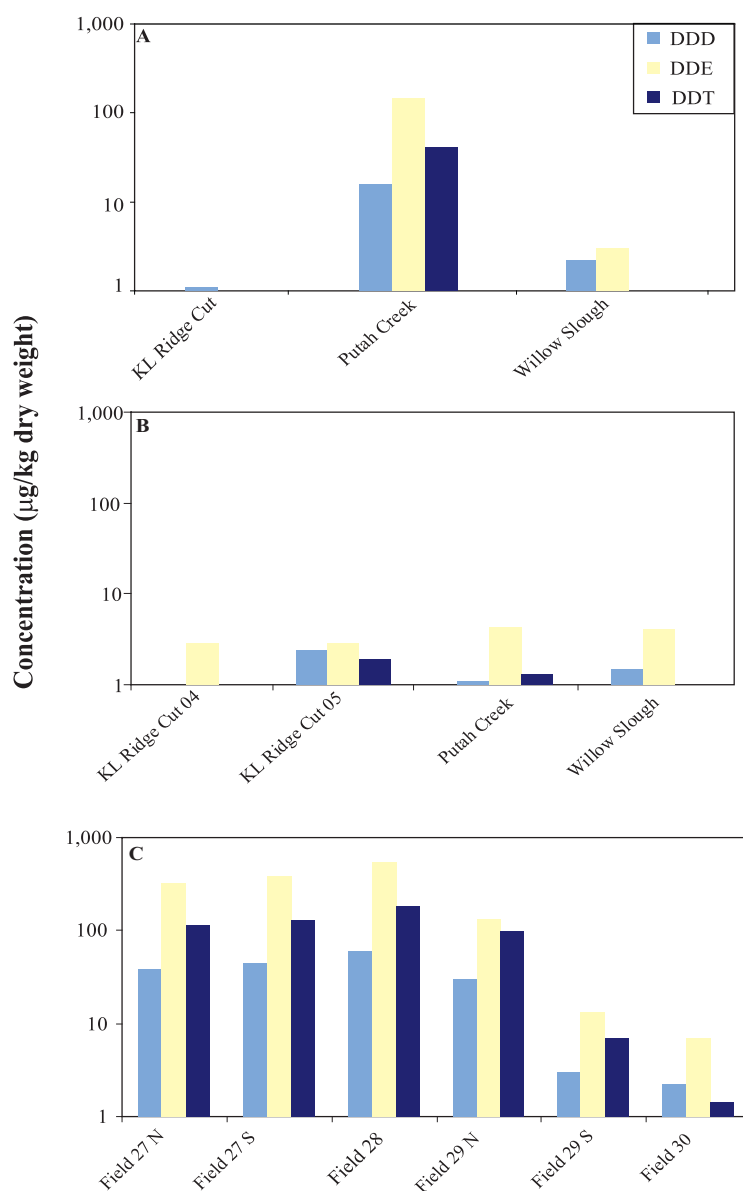

Figure 10. Organochlorine insecticide concentrations in samples collected in 2004 and 2005 from (A) bed sediments, (B) suspended sediments, and (C) soils within the Bypass.

samples along with bed and suspended sediments from Putah Creek ranged from 1.4 to 5.0 and were slightly lower than ratios observed in the San Joaquin River, ranging from 2.3 to 8.8 (Pereira et al. 1996). These ratios are consistent with degradation experiments where DDE/DDT ratios in DDT spiked

soil subjected to long-term weathering were >1 (Hitch and Day 1992). DDD/DDT ratios in the soil samples ranged from 0:3 to >1, indicating the potential for some anaerobic degradation in all soils. Field 30, however, had the highest DDD/DDT and DDE/DDT ratios compared with the other sites, indicating that more active anaerobic and aerobic degradation processes were occurring in the rice field soils. DDE/DDT ratios in soils from fields 27 and 28 were similar to ratios measured in Putah Creek bed sediment and suspended sediment samples. This similarity indicates the potential for resuspension and movement of bed sediments from the creek to the agricultural fields possibly during high-flow events.

Although the use of DDT was banned in 1972, it continues to persist in sediment throughout the Sacramento and San Joaquin River systems. Impurities in commercial dicofol mixtures applied throughout the Central Valley have been a continuing source of DDT to the environment (Pereira et al. 1996). Decreased ratios of DDE to DDT would indicate a source of DDT in the environment; however, in the Yolo Bypass, ratios appear to be similar between soils and bed sediments. Also there is no known use of dicofol in the Yolo Bypass or the surrounding watersheds, indicating that there is no new source of DDT in this area. Organochlorine insecticides such as DDT, DDE, and DDD tend to persist in sediment and soils (log $K_{oc} \sim 5.5$) and can cause reproductive impairment in a variety of fish and birds of prey (U.S. Environmental Protection Agency 1988). Recently, DDT, DDE, and dicofol have been implicated as "environmental hormones" that mimic natural hormones causing abnormal sexual development and impaired growth in aquatic organisms (Guillette, Jr. et al. 1994; Colborn et al. 1993). Three recent studies exposed juvenile and adult fish to environmentally-relevant DDE concentrations and observed a delay in sexual maturation, skewed sex ratios in juvenile fish as well as abnormal sexual development (Baatrup and Junge 2001; Bayley et al. 2002; Garcia-Reyero et al. 2006). Continued monitoring of DDTs is needed to ensure the health of the resident fish species within the Yolo Bypass especially juveniles.

CONCLUSIONS

Potential Exposure of Resident Fish to Pesticides

The purpose of this study was to evaluate the potential sources of pesticides to the Bypass, thereby providing information for evaluating pesticide exposure and potential effects on resident fish. A variety of pesticides, including hexazinone and simazine, were present in the dissolved phase, coming in during high flows from watersheds with high agricultural activity. Concentrations of dissolved pesticides are orders of magnitude below levels known to cause acute or chronic toxicity to fish. However, some herbicides do have the potential to decrease primary productivity, thereby reducing the quantity and quality of food available to higher trophic level organisms (Edmunds et al. 1999). For example, the maximum concentration of hexazinone (2.5 µg/L) was similar to the 4-h EC_{50} value (3.2 µg/L) for a natural periphyton community (Schneider et al. 1995).

The pesticides associated with sediments and soils are more hydrophobic than those measured in the water, yet they need to be considered when assessing the total impact to resident fish populations. Again, the concentrations of pesticides associated with the sediments are orders of magnitude below acute toxicity levels for fish. But these pesticides can affect the benthic macroinvertebrates that are considered to be prey items of fish within the Bypass. Pyrethroid insecticides, detected in suspended sediments and soils, are considered to be acutely toxic to an amphipod, *Hyalella sp.*, at very low concentrations (4-10 µg/kg) (Amweg et al., 2005). Concentrations of bifenthrin (~ 2 µg/kg) were slightly below estimated 10 day LC_{50} values for *Hyalella sp.*; however, concentrations of lambda cyhalothrin (6 µg/kg), which is considered the most toxic pyrethroid to amphipods, was above the 10 day estimated LC_{50} value of 4 µg/kg. At this time the LC_{50} of tau-fluvalinate is unknown. The use of pyrethroid insecticides, such as bifenthrin, lambda cyhalothrin, and tau-fluvalinate, is increasing in Northern California and continued monitoring of sediments is needed. Legacy insecticides, such as DDT, DDE, and DDD continue to be of concern because they are known endocrine disruptors.

A complex mixture of low level pesticides were detected in water and sediments as well as in soils collected within the Bypass. Although the concentrations of individual pesticides were well below the acute toxicity levels for fish, exposure to a mixture of pesticides in the water, sediment, and potential prey items could lead to sub-lethal or chronic effects. Therefore, continued monitoring of pesticides in this area is needed to determine the potential risks and ensure the health of the aquatic organisms within the Yolo Bypass throughout the year.

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